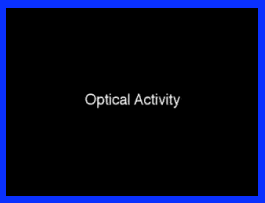
Properties of Chiral Molecules:
Optical Activity

## *Optical Activity*

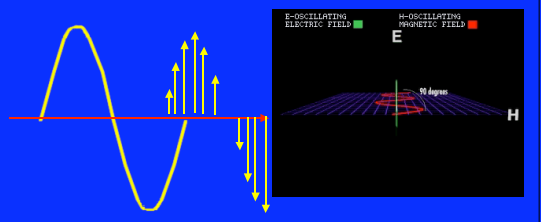



## *Optical Activity*

A substance is optically active if it rotates the plane of polarized light.

In order for a substance to exhibit optical activity, it must be chiral and one enantiomer must be present in excess of the other.

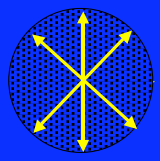
## *Light: electromagnetic radiation*



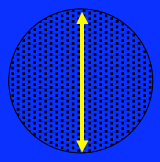

Optical activity is usually measured using light having a wavelength of 589 nm; this is the wavelength of the yellow light from a sodium lamp and is called the D line of sodium.

## *Polarized light*

ordinary (nonpolarized) light consists of many beams vibrating in different planes

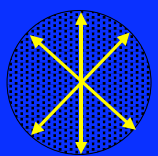


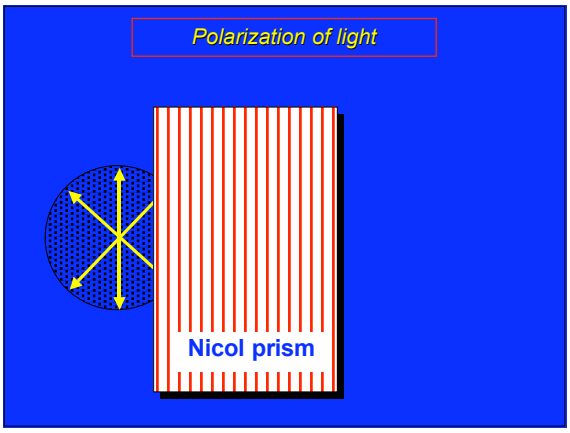
plane-polarized light consists of only those beams that vibrate in the same plane

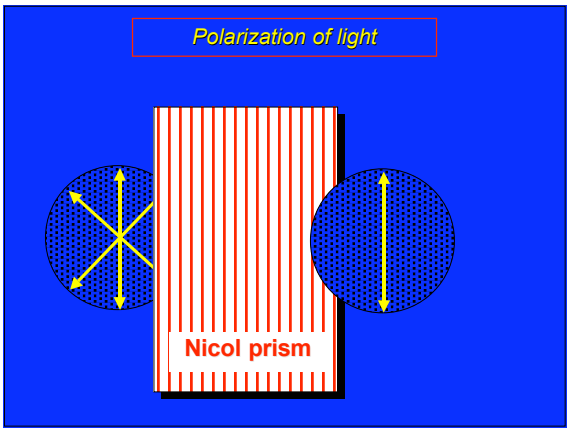


## *Polarization of light*

"White Light"




Polarization of light
Nicol prism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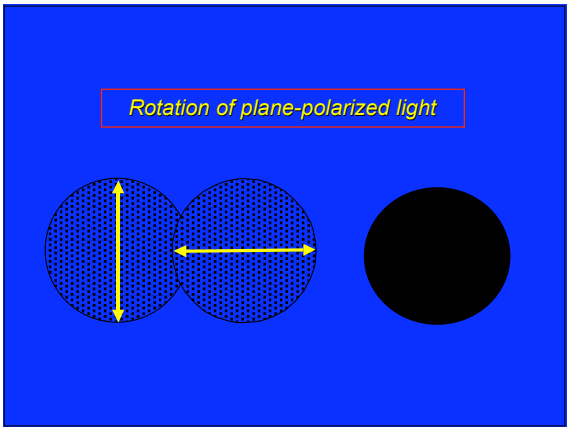
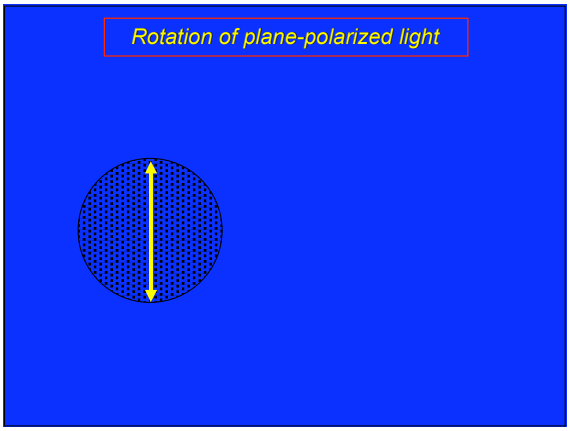

Rotation of plane-polarized light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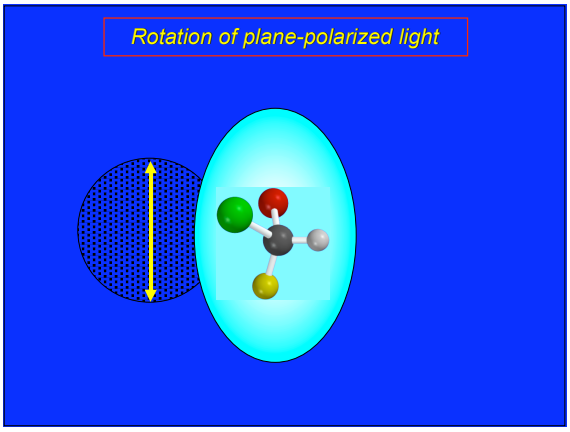
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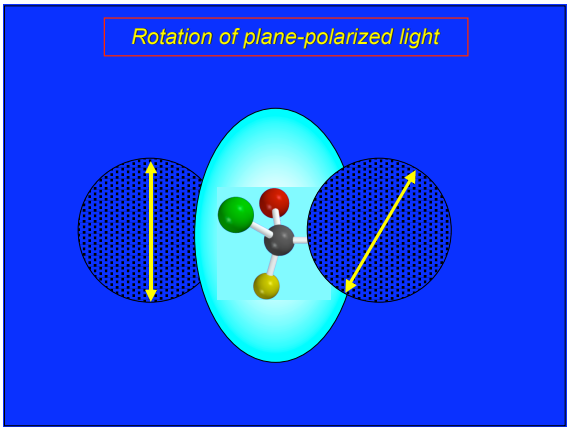
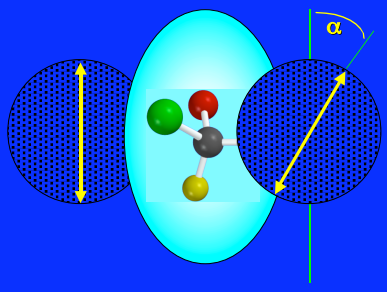
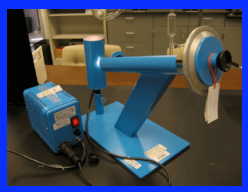

Rotation of plane-polarized light

## *Rotation of plane-polarized light*




## *Measuring the rotation of a chiral molecule: Polarimeter*



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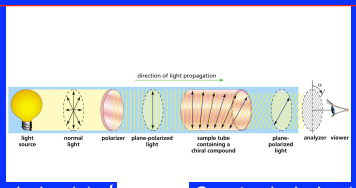


Clockwise (+); *d*

Counterclockwise (-); *l*

Different from absolute (*R,S*) configuration

## *Specific rotation*

observed rotation ($\alpha$) depends on the number of molecules encountered and is proportional to:

path length (*l*), and
concentration (*c*)

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therefore, define specific rotation [$\alpha$] as:

$$[\alpha] = \frac{100\ \alpha}{cl}$$

concentration = g/100 mL
length in decimeters

## *Racemic mixture*

a 50:50 mixture containing equal quantities of *enantiomers* is called a *racemic mixture*

*a racemic mixture is optically inactive*
($\alpha = 0$)

a sample that is optically inactive can be either an achiral substance or a racemic mixture

*Optical purity*

an optically pure substance consists exclusively of a single enantiomer

enantiomeric excess =
% one enantiomer – % other enantiomer

% optical purity = enantiomeric excess

$$\text{optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$$

$= +5.44^{o} / +13.60^{o} \times 100$ =40% *d*-

$$\text{enantiomeric excess} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}} \times 100\%$$

40% *d*- in excess
70% *d*- and 30% *l*-
60% Racemic